Mass Balance of Trace Elements in Walker Branch Watershed: Relation to Coal-Fired Steam Plants

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A mass balance study of trace element flows at the TVA Allen Steam Plant at Memphis showed that most of the released Hg, some Se, and probably most Cl and Br are discharged to the atmosphere as gases. The elements As, Cd, Cu, Ga, Mo, Pb, Sb, Se, and Zn were concentrated in fly ash compared to slag and were more concentrated in the ash discharged through the stack than in that collected by the precipitator, while Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, and Ti showed little preferential partitioning between the slag and the collected or discharged fly ash. The elements Cr, Cs, Na, Ni, U, and V exhibited behavior intermediate between the latter two groups.

This information about stack emissions of trace elements from the Allen Plant was used to estimate the likely range of air concentrations and input (dry and wet deposition) to the Walker Branch Watershed. The watershed, which is on the ERDA reservation at Oak Ridge, is within 20 km of three coal-fired steam plants, two in the TVA system and one belonging to ERDA. The estimated input values are compared to measurements of Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in wet precipitation falling on the watershed during 1973 and 1974. Dry deposition of these elements could not be measured directly but estimates indicated that this could be of the same order of magnitude as the rainwater input. A six-month mass balance indicated that the watershed efficiently retains Pb (97–98% of the atmospheric input), Cd (94–95%), Cu (82–84%), while Cr (69%), Mn (57%), Zn (73%), and Hg (69%) are less well retained.

Introduction

The work reported here was supported by two grants from the National Science Foundation RANN Program. One of these is the Allen Steam

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Plant study and the other is the Ecology and Analysis of Trace Contaminants (EATC) Program. The Allen Steam Plant work involved an investigation of the disposition of trace elements from coal burned at a large TVA Steam Plant, the Thomas A. Allen Plant in Memphis, Tennessee. The EATC Program is a large multidimensional effort involving the development of improved measurement techniques for trace contaminants, environmental studies of the distribution and movement of trace elements in watersheds (including the ERDA Walker Branch Watershed), the development of a unified transport model to simulate the atmospheric dispersion of pollutants and their subsequent deposition and aquatic transport on a watershed scale, development of aqueous abate-

ment techniques for Cd, Zn, CN⁻, Pb, and Hg and support of the Toxic Materials Information Center.

This paper presents appropriately related results from the Allen Steam Plant study, for background information, and preliminary data concerning a 14 month trace element budget for the Walker Branch Watershed. Walker Branch Watershed (WBW) is a hydrologically well calibrated watershed on the ORNL-ERDA reservation, within 20 km of three coal-fired steam plants. The relationship of the emissions from these steam plants to the trace element input at WBW is the primary goal of this discussion.

Allen Steam Plant Results

The Allen Plant, located on the Mississippi River near Memphis, Tennessee, is a 890 MW(e) plant generating power from three similar cyclone-fed boilers. In general, the coal comes from western Kentucky and Illinois and typically contains 3–4% sulfur. Since new precipitators have been recently installed with a mass efficiency of 97–99+%, our study is indicative of a plant employing the best available technology for particulate emission control.

Using a mass balance approach we were able to obtain sufficient data to calculate a budget for some 38 elements (1–4). We also analyzed for trace metals in soil cores at various distances from the plant along a north-south transect (2). From the mass balance results we were able to draw some general conclusions about the behavior of the elements as summarized in Table 1. There is a large group of elements (group 1) which are equally concentrated in the fly ash from the plant and in the boiler bottom slag. Furthermore, these elements show no enrichment or depletion in the fine particulate material compared to the larger particulate material entering the precipitator. This suggested no appreciable vapor-phase transport for these elements. All of these elements except Co and Fe are characterized as lithophilic, i.e., they tend to be associated with aluminosilicate minerals. Co and Fe may be either lithophilic or chalcophilic. All of the elements in group 2 in Table 1 are chalcophilic. That is, they tend to be associated with the sulfide minerals in rocks. Cu may be either chalcophilic or lithophilic. Group 2 elements tend to be enriched in the fly ash compared to the slag and enriched in the smaller particles compared to the large particulates indicating condensation or adsorption from the vapor phase. A substantial fraction of the elements in the third group are found in the vapor phase entering the precipitators.

Table 1. Categories of observed behavior of various elements at the Allen Steam Plant.

Group no.	Class	Elements
1	Equally concentrated in slag and fly ash and not concentrated appreciably in smaller particulates	Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, Ti
2	More concentrated in fly ash than slag and more concentrated in smaller particulates	As, Cd, Cu, Ga, Mo, Pb, Sb, Se, Zn, S
3	Discharged in vapor phase	Br, Cl, probably some F, Hg, Se, S
4	Intermediate between groups 1 and 2	Cr, Cs, Na, Ni, U, V

Although we did not actually measure fluorine in our experiments, we inferred from similarities to Cl and Br and from the literature (5) that it may be in the vapor phase. Selenium is interesting, in that we observed 23% in the vapor phase entering the precipitator while the remainder was associated with the fly ash (3). Since the precipitator efficiently removes particulate matter from the flue gases, about 93% of the selenium emitted from the stack is in the vapor phase. In addition, our measurements show that selenium is in the zero oxidation state both on the fly ash and in the vapor. Group 4 elements behave in an intermediate fashion somewhat between the behavior of group 1 and group 2 elements. Of these, Na, Cs, U, and V are lithophilic, and Cr and Ni may be either lithophilic or chalophilic.

Klein et al. (4) postulate the following explanation for the behavior summarized in Table 1. Trace elements in coal are present in aluminosilicates, as inorganic sulfides or as organic complexes. On combustion at temperatures of 1300-1600°C the aluminosilicates are not decomposed but, rather, melt and coalesce to form slag and fly ash. On the other hand, sulfide and organic compounds are decomposed during combustion, with the elements bound in this form entering the vapor phase. If the elements are dispersed in coal, they remain dispersed when the coal is burned, at least initially. Thus, even those elements which are not thermodynamically stable in any volatile form at the combustion temperature may initially enter the flue gas stream. As the flue gas stream cools, these elements condense or absorb on or react with the fly ash and, hence, tend to be concentrated on the smaller particles which have a higher surface area per unit mass compared to larger particles. Since the slag is in contact with the flue gas for a short

time at a high temperature, condensation on the slag is minimal.

Recent results obtained by Jorde, Kaakinen, and their colleagues at the University of Colorado on a pulverized coal unit burning low sulfur western coal indicated very similar behavior for the elements as discussed above (6–8). Therefore, this categorization may be more general than we could have hoped to expect. From these studies we believe we can say a good deal about trace element emissions from any steam plant given data on the trace element content of the coal burned, the plant operating conditions and the nature of pollution abatement operations.

From the emission rates measured at Allen, maximum ambient air concentrations for the region near the plant were calculated assuming severe meteorological conditions; these were compared to proposed . ambient air standards. The results for a few of the elements are shown in Table 2. The atmospheric dispersion model and the calculations made by use at this model are described by Bolton et al. (2). The standards used were either those of EPA (for Be and Hg) or the industrial workroom standards of the American Conference of Government Industrial Hygenists. The latter were arbitrarily divided by 100 to convert to ambient air standards.* The results show that even for the severe meteorological conditions the standard is never exceeded, and there is usually a safety factor of 10 or more (on a yearly average basis there is a safety factor of many orders of magnitude).† Obviously, one can imagine the case of a much larger plant with lower stacks (the stacks at Allen are 122 m) and burning a coal more enriched in trace elements than we observed at Allen. Under such an extreme situation the ambient air standard for various elements could be exceeded. However, it would appear that if the particulate emission controls are as good as at Allen and tall stacks are used, ambient air concentrations of trace elements

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*An ambient air standard can be derived from the industrial hygiene standard by merely reducing the latter to account for the difference between 8 hr/day exposure for 225 days per year and an exposure for 24 hr/day for 365 days per year. This would be a factor of 4.86. We might also add an additional safety factor of 10 to account for the more susceptible individuals of the public. The total factor would be 48.6. Hence, reducing the industrial hygiene value by a factor of 100 appears to be reasonably conservative.

†The severe meteorological conditions correspond to a stability class A and a undirectional wind of 10 m/sec for an extended period of time. The maximum air levels given in Table 2 correspond to the maximum ground level concentration in the downwind direction calculated for these conditions. If there were also an inversion lid confining the plume the concentrations might be double those given in Table 2.

Table 2. Calculated ambient air concentrations around the Allen Steam Plant as compared with ambient standards.

| Element | Concentration, $\mu g/m^3$ | | Concentration/standard | |
	Maximum Instantaneous air level	Air standard[a]	Short time period	Maximum yearly avg[b]
As	0.13	5	0.026	4.4×10^{-5}
Be	0.0033	0.01	0.3	5.6×10^{-4}
Cd	0.015	~ 1	0.015	2.4×10^{-5}
Hg	0.0025	1	0.025	4.8×10^{-p5}
Ni	0.22	~10	0.02	3.8×10^{-5}
Pb	0.19	~ 1.5	0.13	2.1×10^{-4}
Se	0.16	~ 2	0.08	1.7×10^{-4}
Zn	1.7	~50	0.034	5.6×10^{-5}

[a]Based on EPA or ACGIH standards. The values for Be and Hg are EPA ambient air standards. The values for the other elements are the ACGIH workroom TLV's divided by a factor of 100.

[b]These values are based on the maximum yearly average ambient air concentration calculated in the vicinity of the plant.

due to coal combustion can be kept at "acceptable" levels. The problem at Allen is, of course, sulfur. The same test indicates that under adverse meteorological conditions the sulfur dioxide standard would be exceeded.

Concerning long-term accumulation of trace elements in soil surrounding the plant, we saw no evidence of enrichment in soil cores which could be ascribed to the plant. In Table 3 soil concentrations of a number of elements are compared to fly ash composition. These results show that only for a few elements are fly ash concentrations greater than those in soil by a factor of 10 or more. None were enriched by a factor of 100 or greater. We calculated that a factor of at least 100 would have been necessary for us to have observed an enrichment even in the top one cm of soil due to emissions over the 14 years the plant has been operating (2). This calculation assumes an undisturbed soil upon which fly ash is deposited. The soil around the Allen plant is agricultural and is plowed regularly although we tried to sample at locations where such disturbances would have been minimal.

Walker Branch Watershed Results

With the Allen work as background, we turn to a discussion of the measurement of the input and output of trace elements at the Walker Branch Watershed and the possible influences of neighboring steam plants. The location of WBW relative to the steam plants in the area is shown in Figure 1. The Kingston plant of TVA has a peak capacity of about 1700 MW(e). The stack heights are relatively low (~ 84 m) although two new 304-m stacks are

Table 3. Comparison of elemental concentrations in soils collected along a 40-mile north-south transect through the Allen Steam Plant with world averages for similar type soils and with Allen Steam Plant fly ash.

| Element | Concn in soil near Allen | | World average concn for similar soils, ppm | Fly ash concn range, ppm |
	Range, ppm	Average ppm		
Rb	65–178	133	100	120–650
Cs	2.5–14	7.9	10	15–21
Ba	494–781	656	500	400–3000
Pb	5–100	26	12	149[a]
As	5.1–11.5	9.0	5	27–349[a]
Sb	0.75–2.0	1.3	1	3.2–7
Cu	15–64	28	20	300–1000[a]
Au	0.019–0.055	0.038	<0.1	
Zn	256–711	458	50	1500
Cd	0.3–4.0	1.4	0.5	5.8
Hg	0.018–0.067	0.036	0.07	0.04–0.13
Sc	6.6–22.0	14.1	7	5–29
La	30–56	45.5	50	12–36
Hf	6.7–14.5	11.2	6	
V	71–118	93	100	63–780[a]
Ta	0.8–1.1	0.9	22	1.2–<5
Cr	60–106	84.3	100	200–350
Co	10.5–23.6	15.4	8	25–70
Ce	59–95	84	50	
Eu	0.9–1.5	1.1	~1	1.6–1.8
Th	9–17	13	6	3–23
U	3.5	4	1	7–21
Br	1.7–7	3.3	5	2–10
Mg	$6.5–10.9 \times 10^3$	9.7×10^3	5,000	$5–25 \times 10^3$
Ca	$5.5–11.9 \times 10^3$	7.4×10^3	14,700	$10–20 \times 10^3$
Na	$5.5–10.2 \times 10^3$	7.5×10^3	6,300	$3–7 \times 10^3$
Ti	$2.5–4.1 \times 10^3$	3.4×10^3	4,800	$0.7–4.2 \times 10^3$
Mn	386–799	645	850	200–1000
K	$14–22 \times 10^3$	18.9×10^3	13.8×10^3	$12–20 \times 10^3$
Al	$4.8–7.1 \times 10^4$	6.0×10^4	71×10^3	$60–350 \times 10^3$
Fe	$1.7–5.3 \times 10^4$	3.5×10^4	3.8×10^4	$90–235 \times 10^3$

[a]Can be enriched in fly ash by a factor of 10 or more over soils.

nearing completion. The plant, during the period of our study, was burning coal with a sulfur content of about 2–3%. The precipitator efficiency is no better than about 90–92%. The Bull Run Plant is a 980 MW(e) pulverized coal plant with a stack of 244 m and has been burning low sulfur coal (~1%), so that consequently the precipitator efficiency is only about 85%. The ERDA plant at the Y-12 installation is a steam generator which consumes about 0.15 x 10⁶ tons/yr of coal. Thus, it is only about 6% the size of Bull Run as judged by coal consumption. The precipitator efficiency ranges from about 85 to 98 +%, depending on the power level, and the stack height is 80 m. However, it is located just across the ridge from WBW. The total amount of coal burned by the three plants per year is about 7 x 10⁶ tons.

The watershed (Fig. 2) is approximately a 100 ha catchment. Other details about the watershed have appeared in the literature (9–12). We have collected 14 months of rainfall input data and 6 months of dissolved and particulate stream output measurements for 8 elements (13). Table 4 summarizes the input values for rain. Samples were ob-

tained using a Wong wetfall-dryfall sampler and were collected in preacidified polyethylene containers. No correlation between meteorological variables (such as amount of rain, frequency of rain, wind speed or wind direction) and the measured trace element concentrations in the rain were discovered. It is probably that such correlations require a finer time resolution in the measurements.

We compared our results to a number of studies which have been reported for other watersheds. There is a considerable similarity as indicated in Table 5. Considering the difference in geographical location, anthropogenic sources and other variables, such a good agreement of results was not expected.

We also compared rainwater trace element concentration ratios (using Mn as a reference) with those in fly ash obtained at Allen and with soil values also from the Allen work. The results are shown in Table 6. One can see that these ratios suggest that Cr and possibly Zn have significant soil sources from soil dust. Possibly Cu, Pb, and some Zn might be derived from steam plant emissions
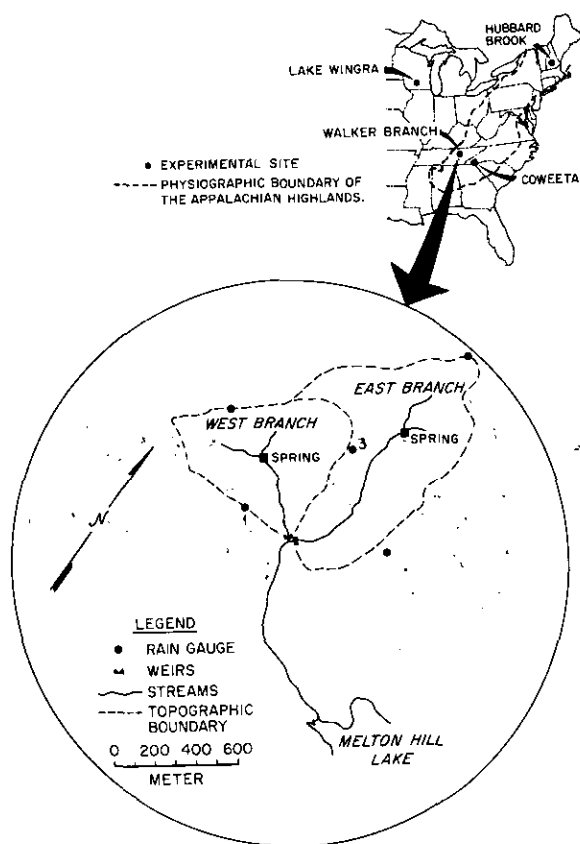
FIGURE 1. Location of neighboring coal-fired steam plants relative to Walker Branch Watershed (WBW).

(see later discussion). Mercury does not appear to be derived from either soil or fly ash sources even if we assume all the Hg condenses on fly ash after leaving the stack. Cadmium might be due to the steam plants if the coal burned had a factor of 3 higher concentration than that observed at Allen.

We also looked at the composition of aerosols at WBW. However, we have data only for one summer month (July 1974). The samples were collected at the weir sites (see Fig. 2), Whatman 41 filter paper being used for the collection surface. Table 7 shows the concentration enrichment ratios of WBW aerosols compared to Allen fly ash using Ce as a basis. The elements of anthropogenic origin can be identified and their relative enrichment over a natural geochemical origin estimated by means of this relative enrichment factor (EF). The EF computation is based on an accurate measurement in each sample of a reference element known or suspected to be of natural origin and believed to be relatively inert chemically in the atmosphere (17–19). In our calculations we have chosen Ce because it seems to vary only slightly between soil samples and is nòt enriched in fly ash (4). In addition, of the five possible reference elements suggested by previous workers which we investigated (Al, Ce, Eu, Lu, and Hg), Ce exhibited the least overall sample to sample and temporal variations. Thus if Ce is chosen as the reference element, then the EF for any other element, X, in the aerosol sample can be determined by:

$$EF = \frac{[X]\ aerosol/[Ce]\ aerosol}{[X]\ soil/[Ce]\ soil}$$

Table 4. Metal input in rain to Walker Branch Watershed.

Period	Metal input, g/ha							
	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
1973								
June	6.0	1.2	33.2	—	23.4	5.2	19.3	56.7
July	20.1	1.8	28.4	—	25.9	9.8	24.5	71.6
August	9.3	0.6	5.6	0.04	7.2	3.8	7.8	22.5
September	12.3	1.1	8.0	0.07	12.6	4.9	10.2	26.4
October	12.3	1.3	8.4	0.12	14.0	4.8	10.3	23.7
November	31.2	10.7	22.4	0.33	39.9	13.4	26.0	49.7
December	11.1	7.5	8.0	1.20	58.0	9.5	49.6	39.0
1974								
January	23.7	8.4	51.8	0.32	47.6	20.0	34.1	46.6
February	12.9	4.1	23.4	0.47	16.5	10.6	6.7	42.0
March	8.4	2.2	20.2	0.16	29.0	14.9	21.6	35.5
April	3.3	0.6	14.8	0.15	5.5	5.8	15.4	35.4
May	7.8	1.2	23.9	0.36	11.5	4.8	26.5	62.7
June	6.3	1.0	6.1	0.05	3.8	2.0	11.1	22.6
July	1.7	0.5	6.5	0.04	4.4	0.9	7.9	16.8

Table 5. Comparison of trace element input by rain between four different areas.

	Trace element input, g/ha-monthly							
	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Avg. for 32 stations in the U.S.[a]	—	—	16.3	—	—	3.2	25.0	74.4
Avg. for 8 stations in Delaware Watersheds[b]	6.9	—	3.0	0.1	—	—	5.2	—
Northwest England[c]	<21.0	3.4	27.3	<0.25	9.7	<7.2	<16.3	101.0
This study	12.8	3.0	19.3	0.27	21.1	7.6	20.5	41.6

[a]Data of Lazrus et al. (14).
[b]Data of Biggs et al. (15).
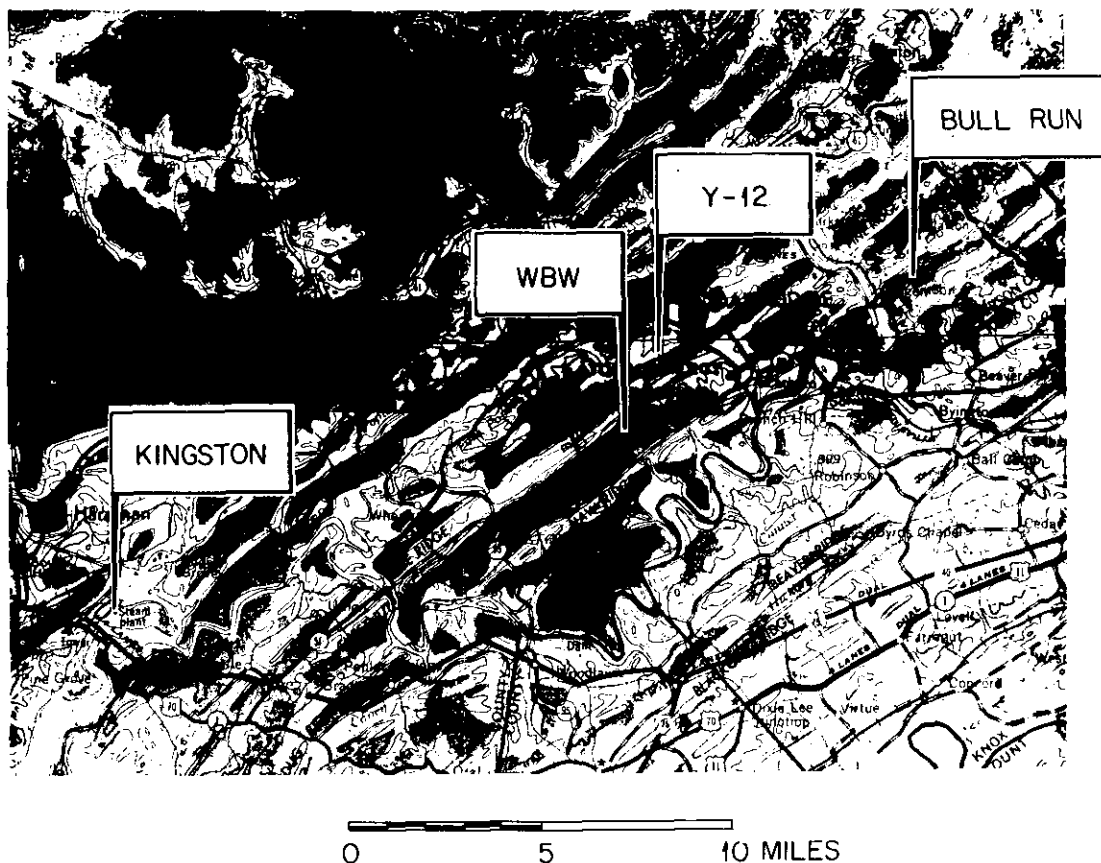[c]Data of Cawse and Peirson (16).

FIGURE 2. Map of Walker Branch watershed study area, indicating stream and precipitation sample sites.

The result of this normalization process is that elements which are soil-derived will have enrichment factors near unity (0.3–1.7, due to the measured variations in Ce concentration) while contaminant elements will have factors ranging up to several orders of magnitude. Thus, if enrichment values for a particular element are much greater than unity and are similar for fly ash and for the aerosol then

Table 6. Elemental ratios in Walker Branch Watershed rain, soil, and fly ash.

	Cd/Mn	Cr/Mn	Cu/Mn	Hg/Mn	Pb/Mn	Zn/Mn
Rain	0.39	0.11	1.5	0.01	1.8	3.8
Soil[a]	0.002	0.13	0.043	6×10^{-5}	0.04	0.7
Fly Ash[b]	0.12	2.1	1.1	1×10^{-4}	1.5	14

[a]Soil elemental data taken from Bolton et al. (2).
[b]Fly ash data taken from Klein et al. (4).

Table 7. Comparison of enrichment factors between aerosols from Walker Branch Watershed and fly ash collected at Allen Steam Plant.

Element	EF Aerosol	EF Fly ash
Ag	236	—
Al	1.9	0.9
As	35.2	57
Au	35.4	35
Br	982	—
Ca	4.2	1.4
Cd	402	30
Cl	295	—
Co	4.1	5.2
Cr	2.0	4.5
Cs	0.3	1.0
Cu	13.7	35
Eu	1.1	1.0
Fe	1.2	2.9
Hf	0.6	0.4
Hg[b]	504	5800
I	100	—
K	1.6	0.7
La	1.6	0.6
Lu	1.0	—
Mn	1.8	0.4
Na	3.7	0.3
Pb	485	17.5
Rb	1.0	1.1
S	4.8	—
Sc	1.1	1.8
Se[b]	380	2174
Ta	0.5	1.3
Tb	1.0	—
Th	1.1	1.4
Ti	2.7	1.6
V	8.1	13.3
Zn	7.2	9.2

$$^aEF = \frac{[Element] / [Ce] \text{ fly ash or deposit}}{[Element] / [Ce] \text{ soil}}$$

[b]EF here is the sum of particulate plus gaseous effluent. EF for Hg when just the particulate phase is taken into account is ~0.5; for Se it is 160.

Table 8. Comparison of wet and dry deposition for selected elements (July 1974) assuming a deposition velocity of 1 cm/sec.

Element	Wet deposition, g/ha	Dry deposition, g/ha
Cd	4.5	2.1
Cr	0.5	0.45
Cu	6.5	2.1
Hg	0.04	0.1
Mn	4.4	3.6
Pb	7.9	22
Zn	16.8	8.5

In Table 9 the output from the watershed with stream flow is compared to the rainwater input. Stream water samples were collected at the weir for each of the two stream branches. These were then filtered through 0.4μ Nucleopore filters immediately upon collecting and the filtrate was acidified. Both filters (suspended materials) and filtrate were analyzed for the eight elements studied. Analytical details have been given elsewhere (13). For all the elements measured the input is considerably greater than the outflow indicating accumulation on the watershed. The order of retention relative to per cent input is Pb > Cd > Cu > Zn > Hg > Cr > Mn. Note that this calculation only includes the rainwater input. Dry deposition is probably of equal magnitude as discussed above, and, hence the percentage retention of the total magnitude would appear to be even higher than the values given in Table 9. However, this conclusion about retention may be premature until we more adequately sample stream runoff during storm events and until we have quantified stream flow exports of both particulate and dissolved metals over at least one full water year. It may be that the system is in better steady state than these preliminary calculations would indicate.

To further evaluate the importance of the emissions for the neighboring steam plants to the trace element input at the watershed, we made some estimates using the atmospheric transport model (2,20). This model can be used to calculate both dry and wet deposition as well as ambient air concentrations. We assumed two sets of trace element concentrations for the coal burned at the three steam plants (see Table 10), i.e., the Allen average results and the averages obtained by the Illinois Geological Survey (21) for a large number of different coal samples. To get a range of values we also used the Illinois average plus one standard deviation, which, for many elements, particularly Cd, gives a very high value indeed.

The calculated wet and dry deposition rates are compared with observed wetfall input in Table 11.

the steam plants may be a major source of that element during the period sampled. On this basis As, Au, Co, Cu, Se, V, and Zn may be from the steam plants. Again, just as for rainwater, Cd appears very enriched—much more so than the Allen fly ash, at least. Pb is likely derived from automobile emissions especially considering the similarity to Br enrichment values.

We have no good way of measuring dry deposition on the watershed. We can estimate it, however, from the measured concentrations of aerosols and from deposition velocities from the literature. If we use a deposition velocity of 1 cm/sec (which may be low for a forested terrain), we can calculate from the aerosol concentration a dry deposition rate which is on the same order of magnitude as the wet deposition. These results are shown in Table 8.

Table 9. Trace element mass balance for Walker Branch, January—June 1974

Period	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Total wetfall input, g/ha								
January	23.7	8.4	51.8	0.32	47.6	20.0	34.1	46.6
February	12.9	4.1	23.4	0.47	16.5	10.6	6.7	42.0
March	8.4	2.2	20.2	0.16	29.0	14.9	21.6	35.5
April	3.3	0.6	14.8	0.15	5.5	5.8	15.4	35.4
May	7.8	1.2	23.9	0.36	11.5	4.8	26.5	62.7
June	6.3	1.0	6.1	0.05	3.8	2.0	11.1	22.6
6 months	62.4	17.5	140.2	1.51	113.9	58.1	115.4	244.8
Total stream output, g/ha[a]								
January	1.21	3.82	6.78–7.62	0.15	7.38		0.98	20.85–23.17
February	0.64	1.96	3.74–4.32	0.11	14.89	<23.9	0.48	13.90–16.04
March	0.69	1.40	3.60–3.86	0.09	6.29		0.35	9.95–10.57
April	0.53	1.10	4.43–5.01	0.04	9.24	<16.1	0.67	12.01
May	0.27	0.62	1.73–2.75	0.07	15.20	<46	0.17	6.75
June	0.14	0.14	2.81	0.01	6.03	<21	0.08	4.45
6 months	3.5	9.1	23.09–26.37	0.47	59.0		2.9	67.9–73.0
Watershed retention, %[b]								
January	95	55	85–87	53	84		97	50–55
February	95	52	82–84	76	10		93	62–67
March	92	36	81–82	44	78		98	70–72
April	84	83	66–70	73	-68		96	66
May	97	48	89–93	81	-32		99	89
June	98	77	54	80·	-59		99	80
6 months	94	48	82–83	69	48		97	70–72

[a]Dissolved + suspended.
[b]Percentage of wetfall atmospheric input.

Table 10. Concentrations of trace elements in coal used in the air model deposition calculations.

Element	Concn, ppm	
	Allen analyses	Illinois Geogological Survey[a]
Al	10,400	12,900
As	4.4	14
Br	3.7	15
Ca	4,340	7.700
Cd	0.5	2.5 ± 7.6
Co	2.9	10
Cr	18	14 ± 7
Cu	8	15 ± 8
Fe	10,850	19,200
Ga	4.5	3
Hg	0.12	0.2 ± 0.2
K	1,540	1,600
Mg	1,210	500
Mn	34	49 ± 40
Ni	16	21 ± 12
Na	696	500
Pb	4.9	35 ± 44
Se	2.2	2
Ti	506	700
V	28.5	33
Zn	46	272 ± 694

[a]Data of Ruch et al. (21).

In the calculations, a high value of deposition velocity (10 cm/sec) was assumed (corresponding to forest cover), so that the highest of the calculated numbers in Table 11 approach maximum estimates. One can see that the range of observed input of Cd is still considerably greater than the range

calculated from the steam plant emissions, as is also true for Cu and Hg. Certainly some of the lead may be due to coal combustion except that the maximum values observed in rain greatly exceed the range of calculated values. However, the aerosol enrichment ratios for Pb and Br indicate automobile emissions are a likely major source of Pb (Table 6). A substantial fraction of Mn, Cr, Ni, and Zn might be due to the steam plants. However, the rainfall ratios for Cr are similar to those for soil as indicated in Table 5.

The calculated maximum wet deposition rates given in Table 11 are all less than the minimum observed wetfall input. This result may be an indication either that wet deposition is not properly calculated or that the wetfall input measured for many of the elements may not be due primarily to the three steam plants. However, certainly some part of the input is due to coal combustion since we have observed spherical particles (presumably fly ash) on dust collection surfaces. An electron micrograph of a cluster of such particles is shown in Figure 3.

We also have attempted to calculate the observed outflow of cadmium from the watershed given the measured input with rainfall. This attempt uses the Wisconsin hydrologic transport model (22,23) which simulates foliar interception, soil exchange, surface runoff, and soil interflow. The surface runoff and soil interflow move contaminants from the landscape to the stream. Figure

Table 11. Trace element deposition rate on Walker Branch Watershed.

Element	Range of input measured in rainfall, g/ha-month	Deposition rate, g/ha-month			
		Maximum computed dryfall input		Maximum calculated wetfall input	
		Allen Steam Plant analyses	Illinois Geological Survey data[a]	Allen steam Plant analyses	Illinois Geological Survey data
Cd	3.30–31.2	0.2	3	0.006	0.1
Cr	0.50–10.7	6	7	0.2	0.3
Cu	5.60–52.0	3	8	0.01	0.3
Hg	0.04–1.2	0.04	0.1	0.001	0.005
Mn	3.80–58.0	10	30	0.4	1.
Ni	0.90–20.0	5	10	0.2	0.4
Pb	6.70–50.0	2	30	0.06	1.
Zn	17.00–72.00	10	300	0.6	10.

[a]Mean plus one standard deviation used.
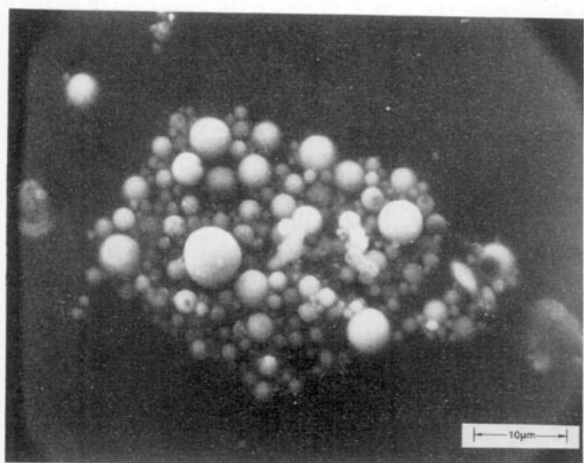
FIGURE 3. Scanning electron photomicrograph of particles deposited on a dust collection surface in Walker Branch Watershed.

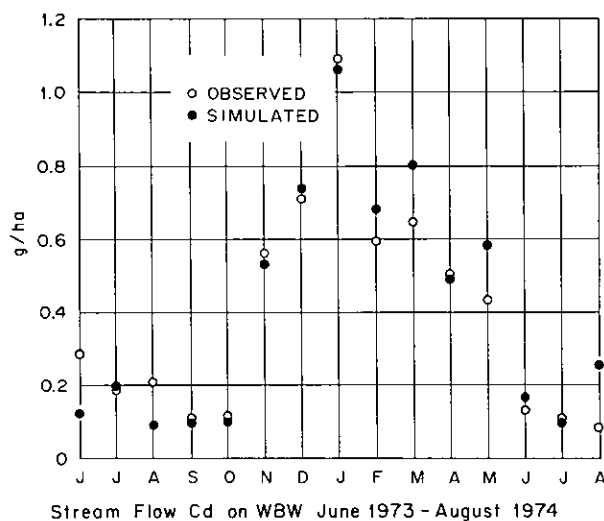Stream Flow Cd on WBW June 1973 – August 1974

FIGURE 4. Observed and simulated outflows of cadmium from Walker Branch Watershed during a 15-month period. The simulation was made using observed wetfall input to WBW and the Wisconsin hydrologic transport model (23).

4 shows the results of this simulation against measured outflow for cadmium for a 15-month period. The simulation is quite good.

The results presented here for WBW must be considered a good beginning. In the future we expect to collaborate with TVA—for example by obtaining monthly composite samples of coal burned at the neighboring steam plants. From trace elemental analyses of these samples we can estimate the trace element emissions more realistically and therefore have better numbers for the models and for comparison to observation at WBW. At the watershed we expect to make routine measurements of aerosol composition by particle size and to measure trace elements outflow during storm events.

Conclusions

Results from the Allen Steam Plant provide a good basis for estimating the behavior of trace elements in coal during combustion. In particular, the behavior of various elements can be categorized depending on whether they are chalcophilic, lithophilic, or tend to form volatile species in the combustion process. From this information one can estimate trace element emissions on the basis of coal analyses and the operational characteristics of the boiler and the emission control equipment. For a plant like Allen with good particulate emission

control and tall stacks, the ambient air concentrations in the steam plant vicinity of trace elements due to the plant appears to be of negligible concern.

Preliminary input-output measurements of eight elements at the Walker Branch Watershed indicate an accumulation on the watershed. The order of retention is $Pb > Cd > Cu > Zn > Hg > Cr > Mn$. Some of the trace element input to the watershed is undoubtedly due to the three nearby steam plants; however, at present the evidence is insufficient to determine what fraction of the input of any given element is due to the plants. All of the results indicate that the input of cadmium is much higher than can be explained by the steam plants.

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